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In-situ X-ray Diffraction on Barium Sulphate using a New High Pressure Flow Cell

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Beamline: X17B1

Introduction: A high pressure flow cell has been designed and commissioned, and angle dispersive XRD data has been collected during the precipitation of barium sulphate under non ambient conditions. The majority of high pressure systems use anvils and presses to obtain high pressures around a small reaction area, however this prototype is unique in that solutions may be examined as they flow through the cell under pressure.

Methods and Materials: The cell is a silicon capillary (length: 1cm, ID: 1mm, wall thickness: 2.6mm) flanked by two steel cones. The cones are made from a corrosion resistant high chrome alloy, Hastelloy C276, to prevent corrosion while flowing high salinity brines through the cell. One of the cones contains a mixing chamber of approximately 1 cubic cm. Two gilson pumps transport the respective solutions to the mixing chamber to form crystals at the desired pressure. These crystals are then transported into the silicon capillary and the direct path of the beam. The pressure of the system is controlled by a pressure regulator on the outlet side of the cell. Pressure transducers monitor pressure, and finally the suspensions are transported to waste.

Experiments were carried out at a pressure of 250 psi and at a beam energy of 30keV. The experiments were designed to monitor the effect of divalent cations and scale inhibitors on the lattice parameters of barium sulphate. Previous work has shown that when calcium was present in the initial reaction mixture, the unit cell parameters of barium sulphate were reduced, due to the formation of a solid solution with the calcium. Addition of magnesium and/or inhibitor increased the levels of calcium incorporation to as much as one fifth of the total cation sites in the crystal. This further reduced the lattice parameters, and it was thought that this could explain increases in inhibitor efficiency in the presence of calcium ions.

In initial commissioning tests, the cell was used to monitor the effect of pressure on the lattice parameters of barium sulphate formed in the presence of additives. Barium sulphate has accurately known crystal d-spacings, so it was practical to calibrate and commission the apparatus using it as a standard. Barium sulphate is orthorhombic, and crystallises in the space group Pnma. Its unit cell parameters are a=8.884, b=5.458 and c=7.153 angstroms.[1]

20.66g/l of $BaCl_2$ and 12.4g/l of Na_2SO_4 were mixed in the cell to form a 1 percent solution of $BaSO_4$. 103.64g of $CaCl_2$ was then mixed with 20.66g/l of $BaCl_2$ and 12.4g/l of Na_2SO_4 for a short case study, designed to determine the effect of calcium on the barium sulphate lattice. Then, based on normal seawater sulphate concentrations and relatively high sulphate scaling formation barium concentrations, scaling brines were mixed in a ratio of 35:65 respectively. These brines represent typical oilfield reservoir concentrations, and therefore results obtained at these relatively low concentrations will have many important applications.

Results: it was found that lattice compression did occur, and the unit cell parameters were reduced from a=8.884, b=5.458and c=7.153 angstroms for pure barium sulphate to a=8.757, b=5.4422 and c=7.035 angstroms. Peak positions were easily ascertained from the crystals obtained on mixing the lower concentration scaling brines, so this experimental setup may be used to determine the effect of additives on barium sulphate precipitation at realistic concentrations.

Conclusions: Angle dispersive XRD was carried out using a new pressure flow cell, and barium sulphate was used to calibrate and commission the detector and cell respectively.

The presence of calcium ions in the reacting solutions was found to cause compression in the barium sulphate lattice. These results are in accordance with previous tests carried out on a conventional laboratory source under ambient conditions, and therefore validate the cell design and experimental development.

Precipitation of barium sulphate was successfully monitored using realistic oilfield concentrations. The level of barium sulphate present in the suspension is considerably lower than concentrations detected by conventional XRD sources.

This cell, which is pressure tested up to 6000 psi, will be used to monitor the effects of additives and pressure on crystallising systems.

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References:

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2. Hennessy, A.J.B., Graham, G.M., Journal of Crystal Growth, 2001 (in press).